

**PATENT ABSTRACTS OF JAPAN**

(11)Publication number : 2002-265573

(43)Date of publication of application : 18.09.2002

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(51)Int.Cl. C08G 61/08

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(21)Application number : 2001-072296

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(22)Date of filing : 14.03.2001

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**(54) FUNCTIONAL GROUP-CONTAINING CYCLOOLEFIN-BASED POLYMER AND ITS MANUFACTURING METHOD****(57)Abstract:**

**PROBLEM TO BE SOLVED:** To provide a polymer having a functional group at one terminal of a cycloolefinic polymer by subjecting a cycloolefinic monomer to metathetical polymerization in the presence of a chain transfer agent having a functional group, and a block copolymer by the copolymerization with MMA or styrene with the use of the polymer.

**SOLUTION:** The cycloolefinic polymer is produced by metathetical polymerization and has a functional group to be represented by the formula:  $\text{CH}_2=\text{CH}-\text{Z}_1-\text{Q}_1$  or  $\text{CH}_2=\text{CH}-\text{Z}_2-(\text{Q}_2)(\text{Q}_3)$  which is derived from a chain transfer agent at one terminal alone. The block copolymer using the polymer and its manufacturing method are also described.

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**LEGAL STATUS**

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

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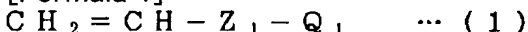
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## CLAIMS

[Claim(s)]

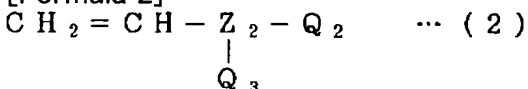
[Claim 1] The cycloolefin system polymer which is a cycloolefin system polymer by the metathesis polymerization, and has a functional group originating in the chain transfer agent shown only in a piece end a general formula (1) or (2).

[Formula 1]



(Z1 expresses O or S among a formula, and Q1 expresses a functional-group end alkyl chain.)

[Formula 2]

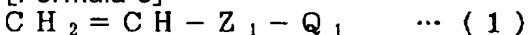


(Z2 expresses N among a formula and Q2 and Q3 express a functional-group end alkyl chain.)

[Claim 2] The cycloolefin system polymer which has a functional group only at the piece end according to claim 1 characterized by a cycloolefin system polymer being a polymer of norbornene and its derivative.

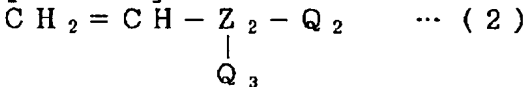
[Claim 3] The manufacture approach of a cycloolefin system polymer of having a functional group for a cycloolefin system monomer only at the piece end by the metathesis polymerization under existence of at least one sort of chain transfer agents shown in a general formula (1) or (2).

[Formula 3]



(Y1 expresses O or S among a formula, and Q1 expresses a functional-group end alkyl chain.)

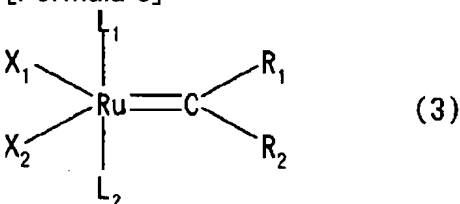
[Formula 4]



(Z2 expresses N among a formula and Q2 and Q3 express a functional-group end alkyl chain.)

[Claim 4] The manufacture approach of a cycloolefin system polymer of having a functional group only at the piece end according to claim 3 characterized by performing a metathesis polymerization to the bottom of at least one sort of the ruthenium system complex compound catalyst expressed with general formula (3) - (6) of existence.

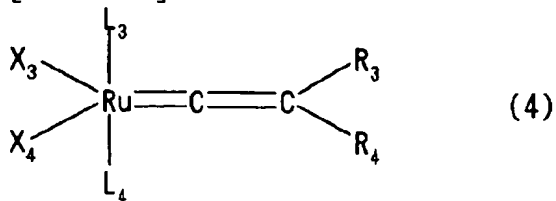
[Formula 5]



the inside of a formula (3), and R1 and R2 are the same -- or -- differing -- hydrogen and the alkenyl radical of carbon numbers 2-20 -- The alkyl group of carbon numbers 1-20, the aryl group of carbon numbers 6-20, the carboxyl group of carbon numbers 2-20, The alkoxy group of carbon numbers 2-20, the alkenyloxy radical of carbon numbers 2-20, The aryloxy group of carbon numbers 6-20, the alkoxy carbonyl group of carbon numbers 2-20, the alkylthio group of carbon numbers 2-20, or a ferrocene derivative is expressed. These The alkyl group of carbon numbers 1-5, a halogen atom, and the phenyl permuted by the alkoxy group of carbon numbers 1-5

may permute if needed. X1 and X2 are the same -- or it differs, an anionic ligand is meant and L1 and L2 are the same -- or it differs, and a neutral electron donor is meant, and 2 of X1, X2, and L2 or three pieces may form a multi-seat chelation ligand together further again.

[Formula 6]



the inside of a formula (4), and R3 and R4 are the same -- or -- differing -- hydrogen and the alkenyl radical of carbon numbers 2-20 --

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the block copolymer and its manufacture approach of the cycloolefin system polymer which has a functional group only at the new piece end, the cycloolefin system polymer which has this functional group, and other polymers.

[0002]

[Description of the Prior Art] It is known that it is the resin ingredient which has the description which was excellent as optical materials, such as an optical disk base, as the norbornene system polymer is indicated by JP,5-39403,A, and the optic formed by the norbornene system polymer is excellent in transparency, thermal resistance, low hygroscopicity, low form birefringence, a moldability, etc. however, since a frame is polyolefine structure, a norbornene system polymer has the low compatibility of a general-purpose polar polymer, for example, acrylic resin etc., and compound-izing with other ingredients and adhesion are difficult for it -- etc. -- there was a problem.

[0003] Composition of the polymer which carries out the metathesis polymerization of the cyclo-octadiene under existence of the chain transfer agent which has a functional group as opposed to this problem, and has a functional group in both ends is reported (C. W.Bielawski et al., Macromolecules2000, 33,678-680). The block copolymer of an ABA mold is compoundable by performing copolymerization-ization with MMA and styrene using this.

[0004] If a chain transfer agent is generally added in a metathesis polymerization system, the molecular weight of the polymer obtained with the addition is controllable. Or more at least one carbon to carbon bond exists between double association which exists in the molecule with the same functional group which exists in the chain transfer agent currently indicated by the above-mentioned reference. Although such a chain transfer agent does not have a bad influence on a metathesis polymerization, the chain transfer agent which reactivity generally added since it was low as compared with a polymerization nature cycloolefin does not work effectively. Therefore, there was a problem of being inefficient-like, about composition of oligomer especially with low molecular weight.

[0005]

[Problem(s) to be Solved by the Invention] The purpose of this invention is using this by the polymer which carries out the metathesis polymerization of the cycloolefin system monomer in view of the trouble of the above-mentioned conventional technique under existence of the chain transfer agent which has a functional group, and has a functional group at the piece end of a cycloolefin system polymer compounding to offer the block copolymer of AB mold by copolymerization-izing with MMA and styrene.

[0006]

[Means for Solving the Problem] By carrying out the metathesis polymerization of the cycloolefin system monomer under existence of the specific chain transfer agent which has a functional group, as a result of inquiring wholeheartedly, in order that this invention persons may conquer the trouble which the conventional technique has A header and this invention were completed for that the cycloolefin system polymer which has a functional group only at the piece end can be obtained, and a block copolymer with an other type polymer being easily obtained on the basis of a header and the piece end functional group of the polymer obtained further.

[0007] That is, according to invention of the 1st of this invention, it is a cycloolefin system polymer by the metathesis polymerization, and the cycloolefin system polymer which has a functional group originating in the chain transfer agent shown only in a piece end a general formula (1) or (2) is offered.

[0008]

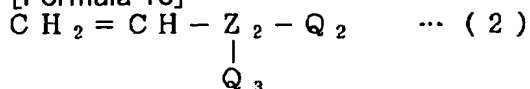
[Formula 9]

$$C H_2 = C H - Z_1 - Q_1 \quad \cdots (1)$$

(Z1 expresses O or S among a formula, and Q1 expresses a functional-group end alkyl chain.)

[0009]

[Formula 10]



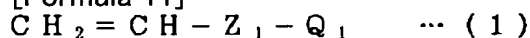
(Z2 expresses N among a formula and Q2 and Q3 express a functional-group end alkyl chain.)

[0010] Moreover, according to invention of the 2nd of this invention, the 1st invention characterized by a cycloolefin system polymer being a polymer of norbornene and its derivative is provided with the cycloolefin system polymer which has a functional group only at the piece end of a publication.

[0011] Moreover, according to invention of the 3rd of this invention, the manufacture approach of a cycloolefin system polymer of having a functional group only at the piece end by the metathesis polymerization is offered in a cycloolefin system monomer under existence of at least one sort of chain transfer agents shown in a general formula (1) or (2).

[0012]

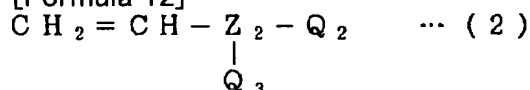
[Formula 11]



(Y1 expresses O or S among a formula, and Q1 expresses a functional-group end alkyl chain.)

[0013]

[Formula 12]

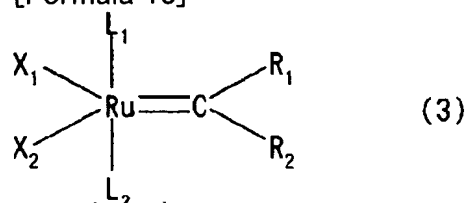


(Z2 expresses N among a formula and Q2 and Q3 express a functional-group end alkyl chain.)

[0014] Moreover, according to invention of the 4th of this invention, the 3rd invention characterized by performing a metathesis polymerization to the bottom of at least one sort of the ruthenium system complex compound catalyst expressed with general formula (3) - (6) of existence is provided with the manufacture approach of a cycloolefin system polymer of having a functional group only at the piece end of a publication.

[0015]

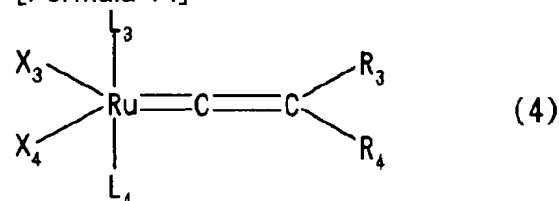
[Formula 13]



[0016] the inside of a formula (3), and R1 and R2 are the same -- or -- differing -- hydrogen and the alkenyl radical of carbon numbers 2-20 -- The alkyl group of carbon numbers 1-20, the aryl group of carbon numbers 6-20, the carboxyl group of carbon numbers 2-20, The alkoxy group of carbon numbers 2-20, the alkenyloxy radical of carbon numbers 2-20, The aryloxy group of carbon numbers 6-20, the alkoxy carbonyl group of carbon numbers 2-20, the alkylthio group of carbon numbers 2-20, or a ferrocene derivative is expressed. These The alkyl group of carbon numbers 1-5, a halogen atom, and the phenyl permuted by the alkoxy group of carbon numbers 1-5 may permute if needed. X1 and X2 are the same -- or it differs, an anionic ligand is meant and L1 and L2 are the same -- or it differs, and a neutral electron donor is meant, and 2 of X1, X2, L1, and L2 or three pieces may form a multi-seat chelation ligand together further again.

[0017]

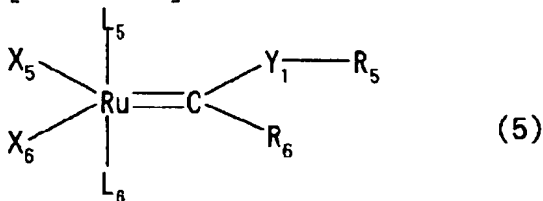
[Formula 14]



[0018] the inside of a formula (4), and R3 and R4 are the same -- or -- differing -- hydrogen and the alkenyl radical of carbon numbers 2-20 -- The alkyl group of carbon numbers 1-20, the aryl group of carbon numbers 6-20, the carboxyl group of carbon numbers 2-20, The alkoxy group of carbon numbers 2-20, the alkenyloxy radical of carbon numbers 2-20, The aryloxy group of carbon numbers 6-20, the alkoxy carbonyl group of carbon numbers 2-20, The alkylthio group of carbon numbers 2-20, the alkyl silyl radical of carbon numbers 2-20, the aryl silyl radical of carbon numbers 2-20, and a ferrocene derivative are expressed. These The alkyl group of carbon numbers 1-5, a halogen atom, and the phenyl permuted by the alkoxy group of carbon numbers 1-5 may permute if needed. X3 and X4 are the same -- or it differs, an anionic ligand is meant and L3 and L4 are the same -- or it differs, and a neutral electron donor is meant, and 2 of X3, X4, L3, and L4 or three pieces may form a multi-seat chelation ligand together further again.

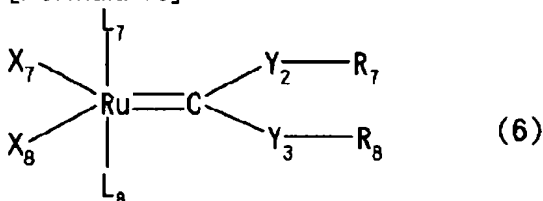
[0019]

[Formula 15]



[0020]

[Formula 16]



[0021] Or it differs. the inside of a formula (5) and (6), and R5, R6, R7 and R8 are the same -- Hydrogen, the alkenyl radical of carbon numbers 2-20, the alkyl group of carbon numbers 1-20, The aryl group of carbon numbers 6-20, the carboxyl group of carbon numbers 2-20, the alkoxy group of carbon numbers 2-20, The alkenyloxy radical of carbon numbers 2-20, the aryloxy group of carbon numbers 6-20, The alkoxy carbonyl group of carbon numbers 2-20, the alkylthio group of carbon numbers 2-20, or a ferrocene derivative is expressed. These The alkyl group of carbon numbers 1-5, a halogen atom, and the phenyl permuted by the alkoxy group of carbon numbers 1-5 may permute if needed. Or differ and sulfur, oxygen, and a selenium element are expressed. Y1, Y2, and Y3 are the same -- Or it differs and an anionic ligand is meant. X5, X6, X7, and X8 are the same -- L5, L6, and L7 and L8 the same -- or it differs, and a neutral electron donor is meant, and X5, X6, X7, X8, L5, L6, two pieces, L7 and L8, or three pieces may form a multi-seat chelation ligand together further again.

[0022] Moreover, according to invention of the 5th of this invention, invention of the 3rd or 4 characterized by cycloolefin system monomers being norbornene and its derivative is provided with the manufacture approach of a cycloolefin system polymer of having a functional group only at the piece end of a publication.

[0023] Moreover, according to invention of the 6th of this invention, invention of the 1st or 2 is provided with the block copolymer characterized by being the copolymer of the cycloolefin system polymer which has a functional group only at the piece end of a publication, and the polymer of other type.

[0024] Moreover, according to invention of the 7th of this invention, the manufacture approach of the block copolymer characterized by making only the piece end of a publication carry out copolymerization of the polymer of other type to invention of the 1st or 2 on the basis of the functional group of the piece end of the cycloolefin system polymer which has a functional group is offered.

[0025] Moreover, according to invention of the 8th of this invention, the 7th invention is provided with the manufacture approach of the block copolymer characterized by the polymerization method of the block copolymer of a publication being living polymerization.

[0026]

[Embodiment of the Invention] This invention is the approach of manufacturing the polymer which has a functional group originating in a specific chain transfer agent only at the piece end, carrying out the polymerization of the polymer which has this functional group only at the piece end further, and other polymers,

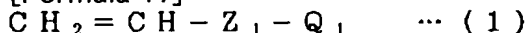
and manufacturing AB mold block polymer, by carrying out the metathesis polymerization of the cycloolefin system monomer under existence of a specific chain transfer agent. Hereafter, this invention is explained to a detail.

[0027] 1. In cycloolefin system polymer this invention which has a functional group only at the piece end, the cycloolefin system polymer which has a functional group only at the piece end can be manufactured by carrying out the metathesis polymerization of the cycloolefin system monomer under existence of a specific chain transfer agent.

[0028] The chain transfer agents which can be used by this invention are at least one sort of chain transfer agents shown in a general formula (1) or a general formula (2).

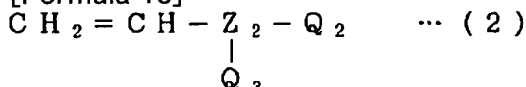
[0029]

[Formula 17]



[0030]

[Formula 18]



[0031] Z1 expresses O or S among a general formula (1), Q1 expresses a functional-group end alkyl chain, Z2 expresses N among a general formula (2), and a functional-group end alkyl chain may be expressed, and Q2 and Q3 may be the same, or they may differ.

[0032] The substituent which has reactivity with other direct functional groups as a functional group here, Or the substituent which can give reactivity by the substituent which a polymerization starts on the basis of there, or deprotection is included. For example, although a halogen radical (a chlorine radical, a bromine radical, fluorine radical), a hydroxyl group, a carboxylic-acid radical, an ester group, the amino group, an acid anhydride radical, a cyano group, a silyl radical, an epoxy group, an acrylic radical, an methacrylic radical, etc. are illustrated, it is not limited to this. As a substituent which can give reactivity by deprotection, an ester group and an acid anhydride radical are desirable.

[0033] As a concrete compound shown by the general formula (1) and (2), the compound which has alpha-halo carbonyl group, alpha-halo benzyl, etc. is mentioned to the vinyl ether frame obtained according to esterification with ethylene glycol mono-vinyl ether and acid halide, for example. Especially in these, 2-BINIROKISHI ethyl dichloro acetate, 2-BINIROKISHI ethyl-2-BUROMO iso butyrate, and 2-BINIROKISHI ethyl-4-chloro methyl benzoate can use preferably.

[0034] The cycloolefin system polymer which has a functional group only at the piece end can be obtained by carrying out the metathesis polymerization of the cycloolefin system monomer under existence of this chain transfer agent.

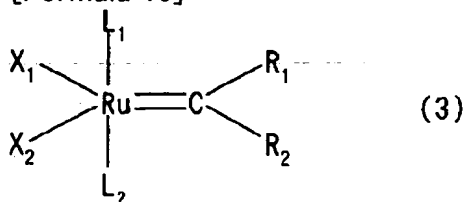
[0035] It is the monomer which consists of annular carbon-carbon bonding as the above-mentioned cycloolefin system monomer, and at least one or more double association exists in the cyclic structure. As the above-mentioned cycloolefin system monomer, since it cannot be used as a reactant polymer which has a functional group at the piece end by the polymer which will be obtained if the monomer of cross-linking is used serving as a bridge formation object, it is not desirable again. However, it can add as a copolymerization component to extent which does not construct a bridge at the time of a polymerization.

[0036] As the above-mentioned cycloolefin system monomer, the monomer which does not have cross-linking with multi-annular unsaturated compounds, such as norbornene and its derivative, a dicyclopentadiene, and its derivative, cyclobutene, a cyclohexene, cyclooctane, cyclo-octadiene, etc. are mentioned. Norbornene and its derivative, and cyclo-octadiene are desirable especially from the field of the effectiveness of polymerization nature, cost, and the polymer obtained.

[0037] If it has metathesis polymerization activity, although there is especially no limit, as a catalyst used for the metathesis polymerization of this invention, it is necessary to decompose, even if a functional group exists, but to maintain activity. it can isolate in air and not so unstable [ moreover / to water ] as such \*\*\*\*\*, -- high -- an activity ruthenium complex compound catalyst is desirable. For example, the ruthenium indicated by U.S. Pat. No. 5,831,108 or an osmium alkylidene complex compound catalyst, the ruthenium complex compound catalyst which was further excellent in thermal resistance, the acid-proof history, and the reaction controllability are mentioned. Especially as a polymerization catalyst of such a property, the ruthenium system complex of the structure of general formula (3) - (6) is desirable.

[0038]

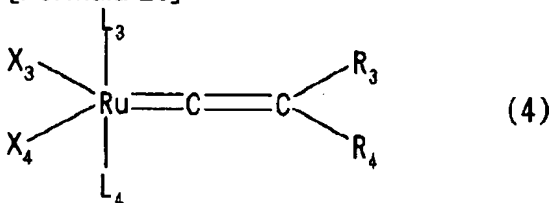
[Formula 19]



[0039] in a general formula (3), R1 and R2 are the same -- or -- differing -- hydrogen and the alkenyl radical of carbon numbers 2-20 -- The alkyl group of carbon numbers 1-20, the aryl group of carbon numbers 6-20, the carboxyl group of carbon numbers 2-20, The alkoxy group of carbon numbers 2-20, the alkenyloxy radical of carbon numbers 2-20, The aryloxy group of carbon numbers 6-20, the alkoxy carbonyl group of carbon numbers 2-20, the alkylthio group of carbon numbers 2-20, or a ferrocene derivative is expressed. These The alkyl group of carbon numbers 1-5, a halogen atom, and the phenyl permuted by the alkoxy group of carbon numbers 1-5 may permute if needed. X1 and X2 are the same -- or it differs, an anionic ligand is meant and L1 and L2 are the same -- or it differs, and a neutral electron donor is meant, and 2 of X1, X2, L1, and L2 or three pieces may form a multi-seat chelation ligand together further again.

[0040]

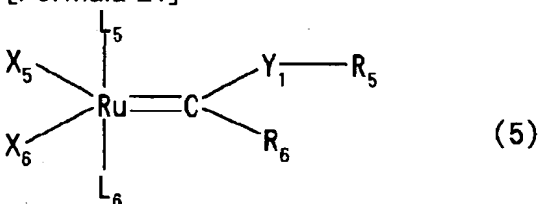
[Formula 20]



[0041] in a general formula (4), R3 and R4 are the same -- or -- differing -- hydrogen and the alkenyl radical of carbon numbers 2-20 -- The alkyl group of carbon numbers 1-20, the aryl group of carbon numbers 6-20, the carboxyl group of carbon numbers 2-20, The alkoxy group of carbon numbers 2-20, the alkenyloxy radical of carbon numbers 2-20, The aryloxy group of carbon numbers 6-20, the alkoxy carbonyl group of carbon numbers 2-20, The alkylthio group of carbon numbers 2-20, the alkyl silyl radical of carbon numbers 2-20, the aryl silyl radical of carbon numbers 2-20, and a ferrocene derivative are expressed. These The alkyl group of carbon numbers 1-5, a halogen atom, and the phenyl permuted by the alkoxy group of carbon numbers 1-5 may permute if needed. X3 and X4 are the same -- or it differs, an anionic ligand is meant and L3 and L4 are the same -- or it differs, and a neutral electron donor is meant, and 2 of X3, X4, L3, and L4 or three pieces may form a multi-seat chelation ligand together further again.

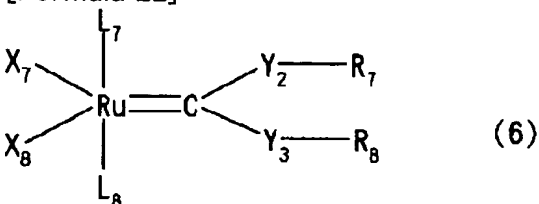
[0042]

[Formula 21]



[0043]

[Formula 22]



[0044] Or it differs. in a general formula (5) and (6), R5, R6, R7, and R8 are the same -- Hydrogen, the alkenyl radical of carbon numbers 2-20, the alkyl group of carbon numbers 1-20, The aryl group of carbon numbers 6-20, the carboxyl group of carbon numbers 2-20, the alkoxy group of carbon numbers 2-20, The alkenyloxy radical



of carbon numbers 2-20, the aryl group of carbon numbers 6-20, The alkyl carbonyl group of carbon numbers 2-20, the alkylthio group of carbon numbers 2-20, or a ferrocene derivative is expressed. These The alkyl group of carbon numbers 1-5, the halogen atom, and the phenyl group permuted by the alkoxy group of carbon numbers 1-5 may permute if needed. Or differ and sulfur, oxygen, and a selenium element are expressed. Y1, Y2, and Y3 are the same -- Or it differs and an anionic ligand is meant. X5, X6, X7, and X8 are the same -- L5, L6, and L7 and L8 the same -- or it differs, and a neutral electron donor is meant, and X5, X6, X7, X8, L5, L6, two pieces, L7 and L8, or three pieces may form a multi-seat chelation ligand together further again.

[0045] In addition, although the complex expressed with general formula (3) - (6) can be manufactured by various approaches, it can compound raw materials, such as a ligand precursor which has L1 - L8 grade, according to a well-known approach, can compound an another side ruthenium complex precursor raw material according to a well-known approach, finally can mix both raw material, and a ligand exchange reaction line can manufacture it.

[0046] As for the metathesis polymerization catalyst which uses the cycloolefin system monomer used by this invention in case a polymer is compounded by the metathesis polymerization, it is desirable that it is 0.0001-1-mol % to all norbornene system monomers. The amount of catalysts has the low rate of polymerization of a norbornene system monomer, and is not desirable less than [ 0.0001 mol % ]. Since it is disadvantageous in cost if it exceeds amount % of one mol of catalysts, it is not desirable. It is the 0.001-0.5-mol range of % more preferably. It is the 0.001-0.05-mol range of % further more preferably.

[0047] Although the reaction temperature in the polymerization method of this invention changes with the melting point of the solvent to be used, and boiling points, it is desirable that it is -30-150 degrees C fundamentally, and the range of it is 10-150 degrees C more preferably. The fluidity of a monomer is low in polymerization temperature being less than -30 degrees C, and it is not desirable when blending an organometallic compound catalyst. On the other hand, if it becomes the temperature exceeding 150 degrees C, since a metathesis catalyst becomes easy to deactivate, it is not desirable.

[0048] Moreover, a monomer, compatibility, or an immiscible solvent can perform the metathesis polymerization system of reaction of this invention, and it can be made to react in ester system solvents, such as ether system solvents, such as halogenation solvents [ , such as aromatic series system solvents such as saturated hydrocarbon system solvents, such as a pentane, a hexane, etc. which have compatibility to a monomer, benzene, and toluene, a methylene chloride, and chloroform ], diethylether, 1, and 2-dimethoxyethane, methyl acetate, and ethyl acetate, the water of a monomer and immiscible nature, and alcohol.

[0049] Although it is desirable to perform the metathesis polymerization reaction of this invention under an inert gas ambient atmosphere, when the stable catalyst of Ru system is used, a polymerization can be carried out in air. Generally the oligomer obtained by the metathesis polymerization reaction has double association, and the oligomer obtained especially with the polymerization method of this invention may deteriorate by the oxygen in air etc. Since this degradation is prevented, it is possible to also make an anti-oxidant add in a polymerization system.

[0050] As an anti-oxidant which can be added, especially if it does not participate in a polymerization reaction, it will not be limited. Especially Pentaerythritol-tetrakis [3-(3-G t-butyl-4-hydroxyphenyl) propionate], 1, 3, 5-trimethyl -2, 4, 6-tris (3, 5-t-butyl-4-hydroxybenzyl) benzene, 2,6-di-tert-butyl-4-methylphenol, tris-(3, 5-G t-butyl-4-hydroxybenzyl) isocyanurate, 1 and 3, and 5-tris (4-t-butyl-3-hydroxy - 2, 6-dimethyl dibenzyl) isocyanurate are desirable.

[0051] Although double association exists in a principal chain at the polymer which has a functional group at the piece end obtained by this invention, it can be made saturation association by hydrogenation. Moreover, an olefin chain can also be saturation-ized for the block copolymer compounded from the polymer which has a functional group at the piece end of this invention by hydrogenation.

[0052] As catalysts for hydrogenation used on the occasion of the above-mentioned hydrogenation, it is manufactured by using Wilkinson complex, cobaltous acetate/triethylaluminum, nickel acetyl acetate / triisobutylaluminum, palladium-carbon, ruthenium-carbon, a nickel-silicious marl, etc., for example. In addition, since the ruthenium system complex of above-mentioned formula (3) - (6) can be suitably used also as catalysts for hydrogenation, when performing a metathesis polymerization using the above-mentioned ruthenium system complex, it can continue at a polymerization and the step of hydrogenation can also be performed continuously.

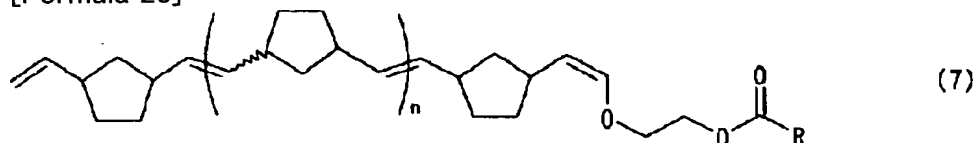
[0053] According to the class of catalyst, the above-mentioned hydrogenation is a homogeneous system or a heterogeneous system, and is usually performed at 0-250 degrees C under the hydrogen pressure of one to 200 atmospheric pressure.

[0054] As a cycloolefin system polymer which has the functional group of this invention only at the piece end, if the above-mentioned 2-BINIROKISHI ethyl dichloro acetate, 2-BINIROKISHI ethyl-2-BUROMO iso butyrate, and 2-BINIROKISHI ethyl-4-chloro methyl benzoate are used as a chain transfer agent, using norbornene as a cycloolefin system monomer, the cycloolefin system polymer which contains the functional group shown in a

structure expression (7) only at the piece end will be obtained, for example.

[0055]

[Formula 23]



(R expresses  $\text{CHCl}_2$ ,  $\text{C}(\text{Me})_2\text{Br}$ , and  $\text{C}_6\text{H}_4\text{CH}_2\text{Cl}$  among a formula.)

[0056] (2) The block copolymer in block-copolymer this invention means a block copolymer with the other type polymer on the basis of the functional group of the cycloolefin system polymer which has the functional group obtained above only at the piece end, i.e., AB mold block copolymer of a cycloolefin system polymer (A) and an other type polymer (B). Although there are specifically copolymerization-izing by the macromolecule reaction using a functional group, copolymerization-ization by the polymerization of other monomer components on the basis of a functional group, etc., since compatibility will fall and the reaction in a homogeneous system will become difficult if the polymer made to react becomes the amount of macromolecules in the case of a macromolecule reaction, copolymerization-izing by the polymerization of other monomer components on the basis of a functional group is desirable.

[0057] At least a radical polymerization, ionic polymerization, and its outcrossing have a radical polymerization industrially advantageous to the polymerization of other monomer components on the basis of an end functional group from the field of the constraint to a polymerization environment, although a polymerization is used. To control of molecular weight and a molecular weight distribution, a living radical polymerization is especially desirable.

[0058] A living radical polymerization is a well-known polymerization method, and the atomic migration mold radical polymerization to which research is advanced energetically recently can be used for it. For example, Matyjaszewski et al., J.Am.Chem.Soc.1995, 117 and 5614, Macromolecules, 1995, 28, 7901 Science 1996, 272, and 866 or Sawamoto et al., Macromolecules The approach currently indicated by 1995, 28, 1721, etc. is used. Though according to this approach a rate of polymerization is generally very high and it is the radical polymerization from which termination reaction, such as coupling of radicals, tends to occur, a polymerization advances in living, the narrow polymer of molecular weight distribution is obtained, and molecular weight can be controlled by the preparation ratio of a monomer and an initiator.

[0059] The poly norbornene-polymethylmethacrylate block copolymer in which methyl methacrylate carried out the polymerization only to the piece end which shows the block copolymer obtained with the above-mentioned structure expression (7) on the basis of the functional group of the poly norbornene which has a functional group, and the poly norbornene-polystyrene block copolymer styrene carried out [ the block copolymer ] the polymerization similarly are mentioned.

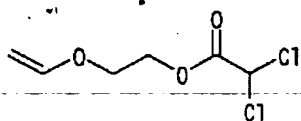
[0060]

[Example] Although an example is given to below and this invention is explained to a detail, this invention is not limited only to these examples. In addition, the chain transfer agent and catalyst which were used in the example were carried out like the next, and were compounded.

[0061] 1. The thing which dissolved synthetic ethylene glycol mono-vinyl ether 5.5g (62.4mmol) of a chain transfer agent in dichloromethane 120ml and pyridine 60ml, and made dichloromethane 30ml dissolve dichloro acetyl chloride 9.19g (62.4mmol) there was dropped, and mixture was stirred at the room temperature for 3 hours. 50ml water was added after that and the reaction was stopped. The organic layer was separated and 50ml ether extracted the water layer twice. Then, it was made to dry with magnesium sulfate with the organic layer separated previously. The brown liquid was obtained by condensing this solution. Vacuum distillation (0.2mmHg, 52 to 55 degree C) of this was carried out, and 6.37g (51% of yield) of chain transfer agents -1 (2-BINIROKISHI ethyl dichloro acetate) shown in a colorless liquefied structure expression (8) was obtained. In addition, NMR, elemental analysis, etc. perform the check of the structure expression, and those values are shown. Moreover, acid halide is changed, by the same approach, the chain transfer agent -2 (2-BINIROKISHI ethyl-2-BUROMO iso butyrate) shown in a structure expression (9) and the chain transfer agent -3 (2-BINIROKISHI ethyl-4-chloro methyl benzoate) shown in a structure expression (10) are compounded, and values, such as NMR and elemental analysis, are shown about a chain transfer agent -3.

[0062]

[Formula 24]

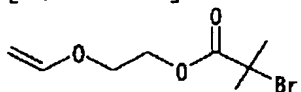


(8)

[0063]  $^1\text{H-NMR}(\text{CDCl}_3)$ :  $\delta$ =6.47 (dd,  $J$ = 14.3, 6.8Hz, 1H,  $\text{CH}=\text{CH}_2$ ), 5.98 (s, 1H,  $\text{CHCl}_2$ ) 4.51–4.48 3.96–3.93 (each m, 4H,  $\text{OCH}_2$ ), 4.21 (dd,  $J$ = 14.3, 2.4Hz, 1H,  $\text{CH}=\text{CH}_2$ ), 4.07(dd,  $J$ = 6.8, 2.4Hz, 1H,  $\text{CH}=\text{CH}_2$ );  $^{13}\text{C}[^1\text{H}]\text{-NMR}(\text{CDCl}_3)$ :  $\delta$ =164.5 (s,  $\text{C}=\text{O}$ ), 151.1 (s,  $\text{CH}=\text{CH}_2$ ) 87.4 (s,  $\text{CH}=\text{CH}_2$ ), 65.4, 65.0 (each s,  $\text{OCH}_2$ ), 64.0(s,  $\text{CHCl}_2$ ); MS,  $m/z$ (rel intensity, %): 198 ( $\text{M}^+-\text{H}$ , 1), 157 (31), 155 (48), 87 (11), 85 (64), 83 (100), 76 (21) 57 (13); elementary analysis calcd for  $\text{C}_6\text{H}_8\text{Cl}_2\text{O}_3$ : C, 36.21; H, 4.05; found: C, 36.46; H, 4.13.

[0064]

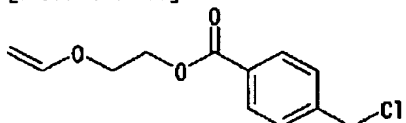
[Formula 25]



(9)

[0065]

[Formula 26]



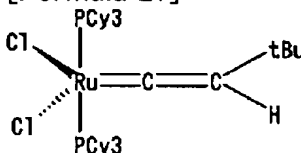
(10)

[0066]  $^1\text{H-NMR}(\text{CDCl}_3)$ :  $\delta$ =8.07–8.04, 7.48–7.45 (each m, 4H,  $\text{C}_6\text{H}_4$ ), 6.52 (dd,  $J$ = 14.5, 6.8Hz, 1H,  $\text{CH}=\text{CH}_2$ ), 4.62 (s, 2H,  $\text{CH}_2\text{Cl}$ ) 4.58–4.55 (m, 2H,  $\text{OCH}_2$ ), 4.24 (dd,  $J$ = 14.5, 2.4Hz, 1H,  $\text{CH}=\text{CH}_2$ ), 4.07(dd,  $J$ = 6.8, 2.4Hz, 1H,  $\text{CH}=\text{CH}_2$ );  $^{13}\text{C}[^1\text{H}]\text{-NMR}(\text{CDCl}_3)$ :  $\delta$ =165.9 (s,  $\text{C}=\text{O}$ ), 151.5 (s,  $\text{CH}=\text{CH}_2$ ) 142.4 (s, C4 of  $\text{C}_6\text{H}_4$ ), 130.2 (s, C 2, 3, and 5, 6 of  $\text{C}_6\text{H}_4$ ) 129.8 (s, C1 of  $\text{C}_6\text{H}_4$ ), 128.5 (s, C 2, 3, and 5, 6 of  $\text{C}_6\text{H}_4$ ) 87.1 (s,  $\text{CH}=\text{CH}_2$ ), 65.8, 63.3 (each s,  $\text{OCH}_2$ ), 45.3(s,  $\text{CH}_2\text{Cl}$ ); elementary analysis calcd for  $\text{C}_{12}\text{H}_{13}\text{ClO}_3$ : C, 59.88; H, 5.44; found: C, 59.61; H, 5.47.

[0067] *t*-butyl acetylene of  $\text{PCy}_3$  of 18.2mmol and 9.1mmol(s) was made to react under a nitrogen air current in a 300ml flask with 150ml toluene for 7 hours to  $\text{Ru}(\text{p-cymene}) \text{Cl}_2$  of 15.57g of synthetic examples of a catalyst (9.1mmol). Reduced pressure removal of the toluene was carried out after reaction termination, and the ruthenium complex compound of a structure expression (11) was compounded by recrystallizing by THF / ethanol system.

[0068]

[Formula 27]

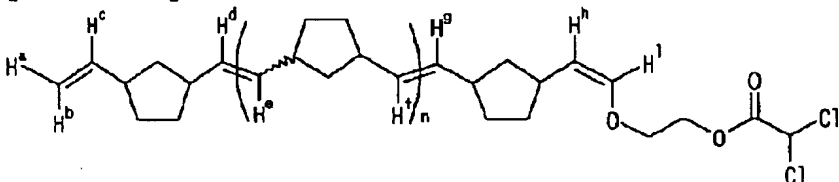


(11)

[0069] It added to 80mg (0.098mmol) of ruthenium system catalysts which show the dichloromethane solution of example 1 norbornene (471mg, 5mmol) and a chain transfer agent -1 (mg [ 99 ], 0.50mmol) with a structure expression (11). The solution of the obtained thin purple was made to react at a room temperature for 52 hours, it flowed into the 150ml methanol after the reaction, and the white solid-state was obtained. The polymer (PNBE-1) which repeats and washes the solid-state of the obtained white with a methanol, is made to dry at a room temperature, and is shown with a structure expression (12) was obtained. Yield was 92%. the obtained polymer -- VPO -- molecular weight distribution according [  $M_n$  according /  $M_n$  by law / to  $2.9 \times 10^3$  and the NMR method ] to  $3.3 \times 10^3$  and GPC analysis were 2.17.  $^1\text{H-NMR}$  shows attribution of each peak below, and the chart of NMR is shown in drawing 1 .

[0070]

[Formula 28]



(12)

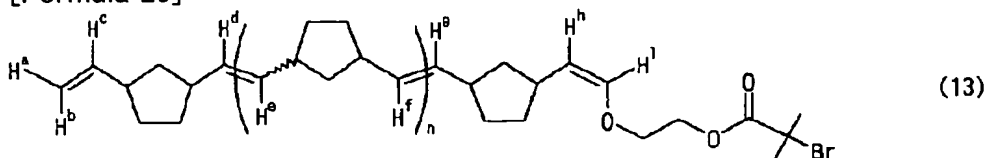
[0071]  $^1\text{H-NMR}(\text{CDCl}_3)$ :  $\delta$  -- 5.98 (s,  $\text{CHCl}_2$ ) and 5.86 (d,  $J$  =6.2Hz,  $\text{H}_i$ ) -- 5.80 (ddd,  $J$ = 17.2, 9.9, 7.3Hz,  $\text{H}_c$ )

5.40–5.29 (m, Hd-g of trans-polymer), 5.24–5.16 (m, Hd-g of cis-polymer), 4.96 (ddd, J= 17.2, 1.3, 1.3Hz, Hb) 4.87 (ddd, J= 9.9, 1.3, 1.3Hz, Ha), 4.45–4.42 (m, OCH<sub>2</sub>) and 4.41 (dd, J= 9.0, 6.2Hz, Hh) -- 3.98–3.95 (m, OCH<sub>2</sub>), 2.82–2.72, 2.50–2.35, 1.92–1.69, 1.43–1.25, 1.12–0.96 (each m, CH and CH<sub>2</sub>).

[0072] The polymer (PNBE-2) which performs the same actuation as an example 1, and is shown with a structure expression (13) was obtained except having added 0.50mmol(s) for the chain transfer agent -2 instead of example 2 chain transfer agent -1. Yield was 94%. the obtained polymer -- VPO -- molecular weight distribution according [ Mn according / Mn by law / to 2.7x10<sup>3</sup> and the NMR method ] to 3.0x10<sup>3</sup> and GPC analysis were 2.49. 1 H-NMR shows attribution of each peak below, and the chart of NMR is shown in drawing 2.

[0073]

[Formula 29]

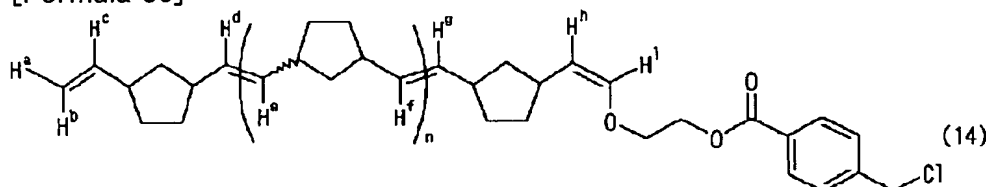


[0074] 1 H-NMR(CDCl<sub>3</sub>): delta 5.88 (dd, J= 6.2, 1.1Hz, Hi), 5.80 (ddd, J= 17.4, 10.3, 7.5Hz, Hc), 5.39–5.28 (m, Hd-g of trans-polymer), 5.22–5.19 (m, Hd-g of cis-polymer), 4.96 (ddd, J= 17.4, 2.0, 1.1Hz, Hb) 4.86 (ddd, J= 10.3, 2.0, 0.9Hz, Ha), 4.38 (dd, J= 9.0, 6.2Hz, Hh), 4.36–4.32, 3.96–3.93 (each m, OCH<sub>2</sub>), 2.84–2.71, 2.50–2.35, 1.90–1.71, 1.45–1.28, and 1.12–0.970 (m, CH and CH<sub>2</sub>) and 1.94 (s, CH<sub>3</sub>).

[0075] The polymer (PNBE-3) which performs the same actuation as an example 1, and is shown with a structure expression (14) was obtained except having added the chain transfer agent -3 0.50 mmols instead of example 3 chain transfer agent -1. Yield was 96%. the obtained polymer -- VPO -- molecular weight distribution according [ Mn according / Mn by law / to 4.0x10<sup>3</sup> and the NMR method ] to 4.0x10<sup>3</sup> and GPC analysis were 2.53. 1 H-NMR shows attribution of each peak below, and the chart of NMR is shown in drawing 3.

[0076]

[Formula 30]

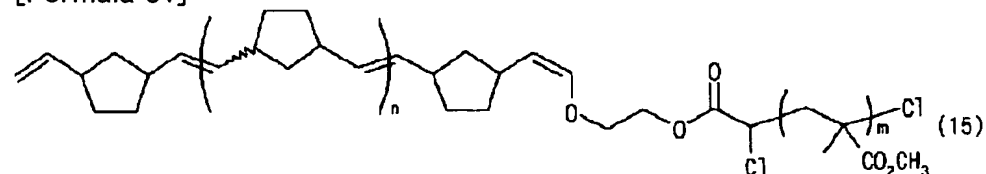


[0077] 1H-NMR(CDCl<sub>3</sub>):delta 8. -- 06 and 7.47 (each d, J= 1.8Hz, C<sub>6</sub>H<sub>4</sub>) -- 5.92 (dd, J= 6.2, 0.9Hz, Hi) 5.80 (ddd, J= 17.4, 10.3, 7.5Hz, Hc), 5.39–5.28 (m, Hd-g of trans-polymer), 5.22–5.19 (m, Hd-g of cis-polymer), 4.96 (ddd, J= 17.4, 2.0, 1.1Hz, Hb) 4.87 (ddd, J= 10.3, 2.0, 0.9Hz, Ha), 4.62 (s, CH<sub>2</sub>Cl) 4.51–4.47 (m, OCH<sub>2</sub>), 4.39 (dd, J= 9.0, 6.2Hz, Hh), 4.05–4.02 (m, OCH<sub>2</sub>), 2.84–2.71, 2.50–2.34, 1.90–1.68, 1.45–1.26, 1.13–0.97 (each m, CH and CH<sub>2</sub>).

[0078] Methyl methacrylate 198mg (1.98mmol) and piece end functionalization poly norbornene 101mg (0.0348mmol) compounded in the example 1 are dissolved in example 4 toluene 1.5ml, and after adding and deaerating 13mg (0.015mmol) of ruthenium system catalysts, and aluminum(OPri)<sub>3</sub> 313mg (0.060mmol) shown with a structure expression (11), it was made to react under a 74-hour nitrogen air current at 80 degrees C. Then, the 100ml methanol was filled with the viscous solution, and white precipitate was obtained. After the methanol repeated and washed this, the vacuum drying was carried out at the room temperature, and the poly norbornene-polymethylmethacrylate block copolymer shown in a structure expression (15) was obtained. Yield was 90%. the obtained polymer -- VPO -- molecular weight distribution according [ Mn according / Mn by law / to 6.7x10<sup>3</sup> and a formula [Mn= ((conversion % monomer xMw monomer) / (initial PNBE-1 concentration +MnPNBE-1))] ] to 7.8x10<sup>3</sup> and GPC were 1.74. The chart of NMR is shown in drawing 4.

[0079]

[Formula 31]

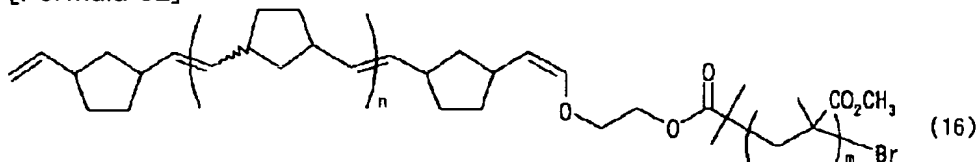


[0080] The poly norbornene-polymethylmethacrylate block copolymer which performs the same actuation as an

example 4, and is shown in a structure expression (16) was obtained except that using the polymer compounded in the example 2 as 5 pieces of examples end functionalization poly norbornene. Yield was 84%. the obtained polymer -- VPO -- molecular weight distribution according [  $M_n$  according /  $M_n$  by law / to  $5.9 \times 10^3$  and a formula  $[M_n = \{(\text{conversion \% monomer} \times M_w \text{ monomer}) / (\text{initial PNBE-2 concentration} + M_n \text{PNBE-2})\}]$  ] to  $6.5 \times 10^3$  and GPC were 1.26. The chart of NMR is shown in drawing 5 .

[0081]

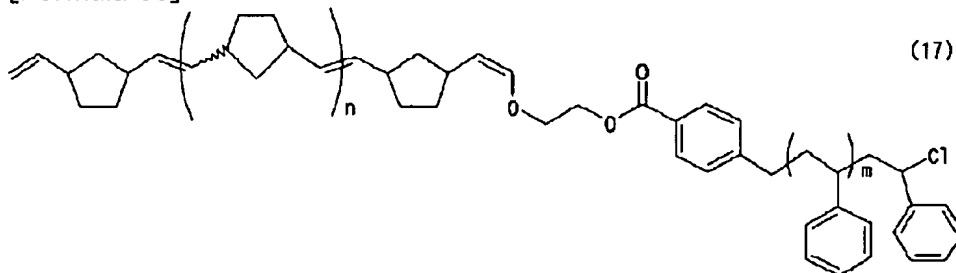
[Formula 32]



[0082] Example 6 styrene 289mg (2.78mmol), toluene 0.1ml, and piece end functionalization poly norbornene 101mg (0.025mmol) compounded in the example 3 were added to CuBr3.6mg (0.025mmol) and 2 and 2'-bipyridine 7.9mg (0.051mmol). The mixture was made to react under a 26-hour nitrogen air current at 90 degrees C. After the reaction, after diluting with 2ml THF, it flowed into methanol 100ml and white precipitate was obtained. After the methanol repeated and washed this, the vacuum drying was carried out at the room temperature, and the poly norbornene-polystyrene block copolymer shown in a structure expression (17) was obtained. Yield was 79%. the obtained polymer -- VPO -- molecular weight distribution according [  $M_n$  according /  $M_n$  by law / to  $10.7 \times 10^3$  and a formula  $[M_n = \{(\text{conversion \% monomer} \times M_w \text{ monomer}) / (\text{initial PNBE-3 concentration} + M_n \text{PNBE-3})\}]$  ] to  $12.3 \times 10^3$  and GPC were 1.80. The chart of NMR is shown in drawing 6 .

[0083]

[Formula 33]



[0084]

[Effect of the Invention] As explained above, this invention can obtain the new block copolymer to which the polymerization of other polymers was carried out on the basis of the functional group about the cycloolefin system polymer which has a functional group only at the new piece end from the cycloolefin system polymer which has a functional group only at this piece end. These new polymers can be used for various applications, and the application is especially expected as a new optical material.

[Translation done.]

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DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1] It is the chart of the NMR spectrum of the polymer manufactured in the example 1.

[Drawing 2] It is the chart of the NMR spectrum of the polymer manufactured in the example 2.

[Drawing 3] It is the chart of the NMR spectrum of the polymer manufactured in the example 3.

[Drawing 4] It is the chart of the NMR spectrum of the polymer manufactured in the example 4.

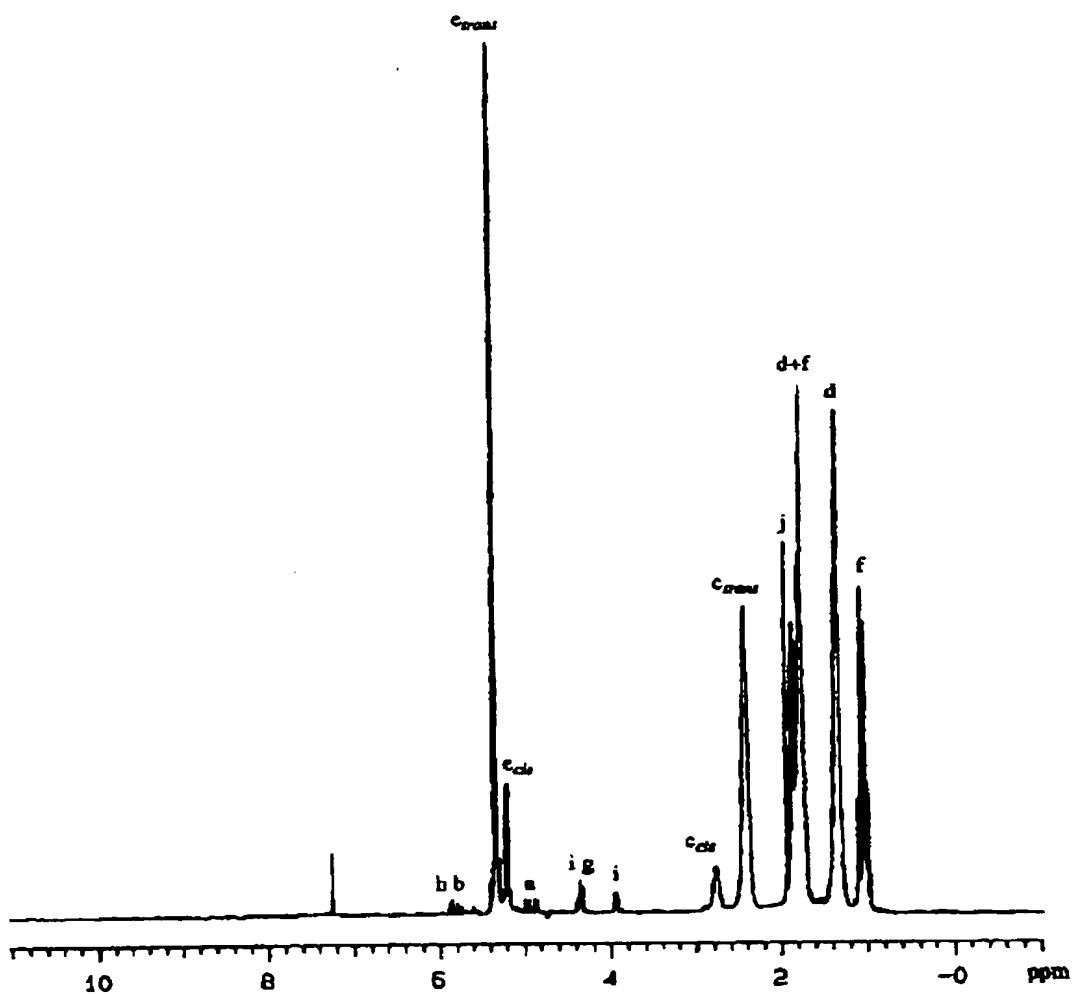
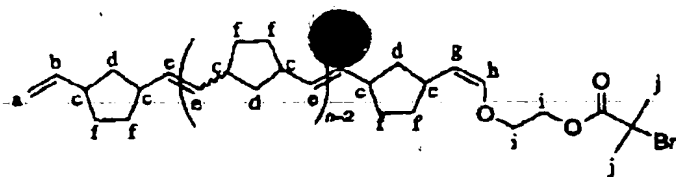
[Drawing 5] It is the chart of the NMR spectrum of the polymer manufactured in the example 5.

[Drawing 6] It is the chart of the NMR spectrum of the polymer manufactured in the example 6.

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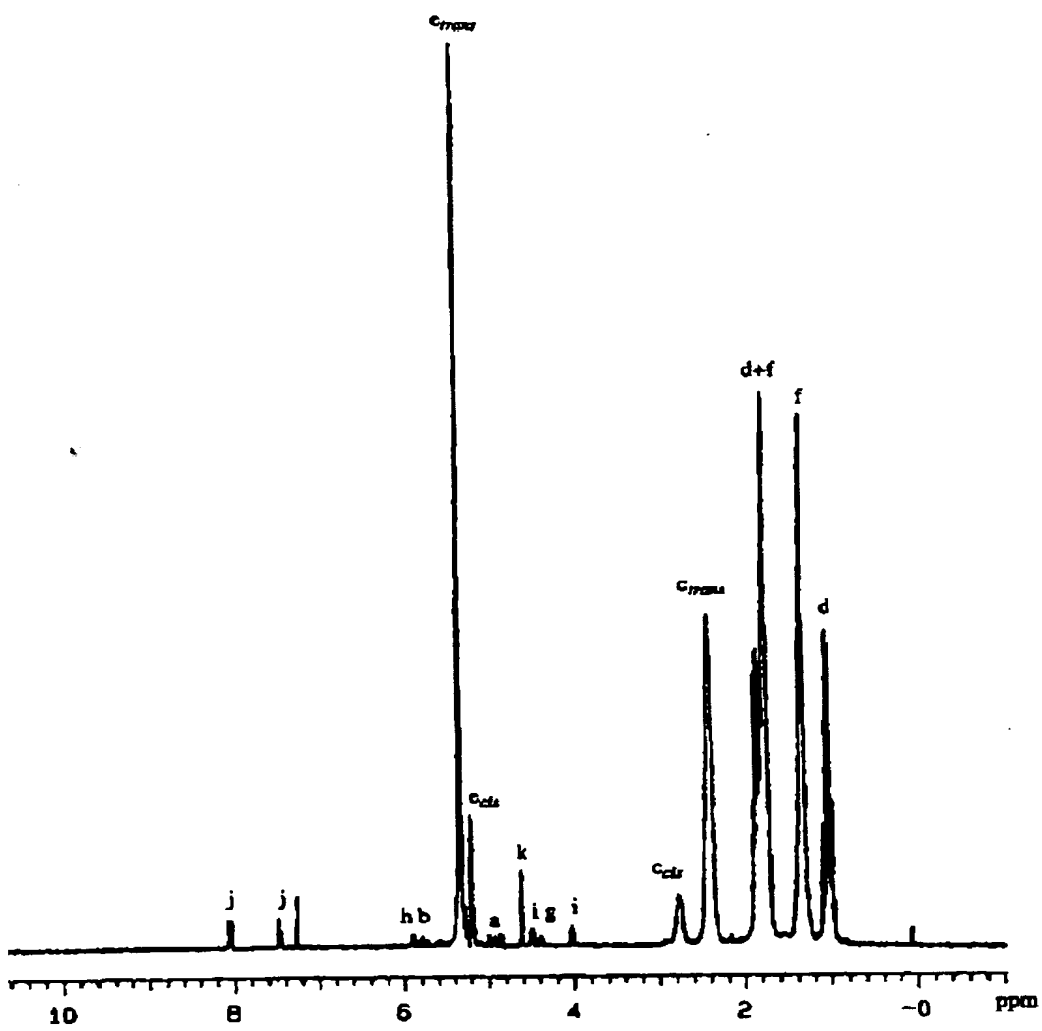
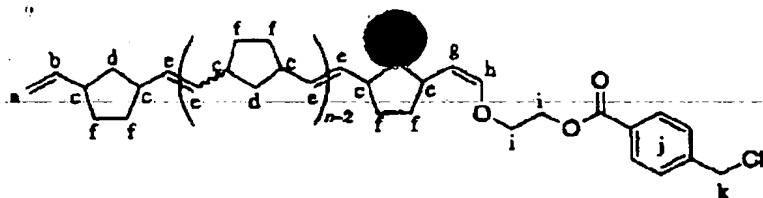
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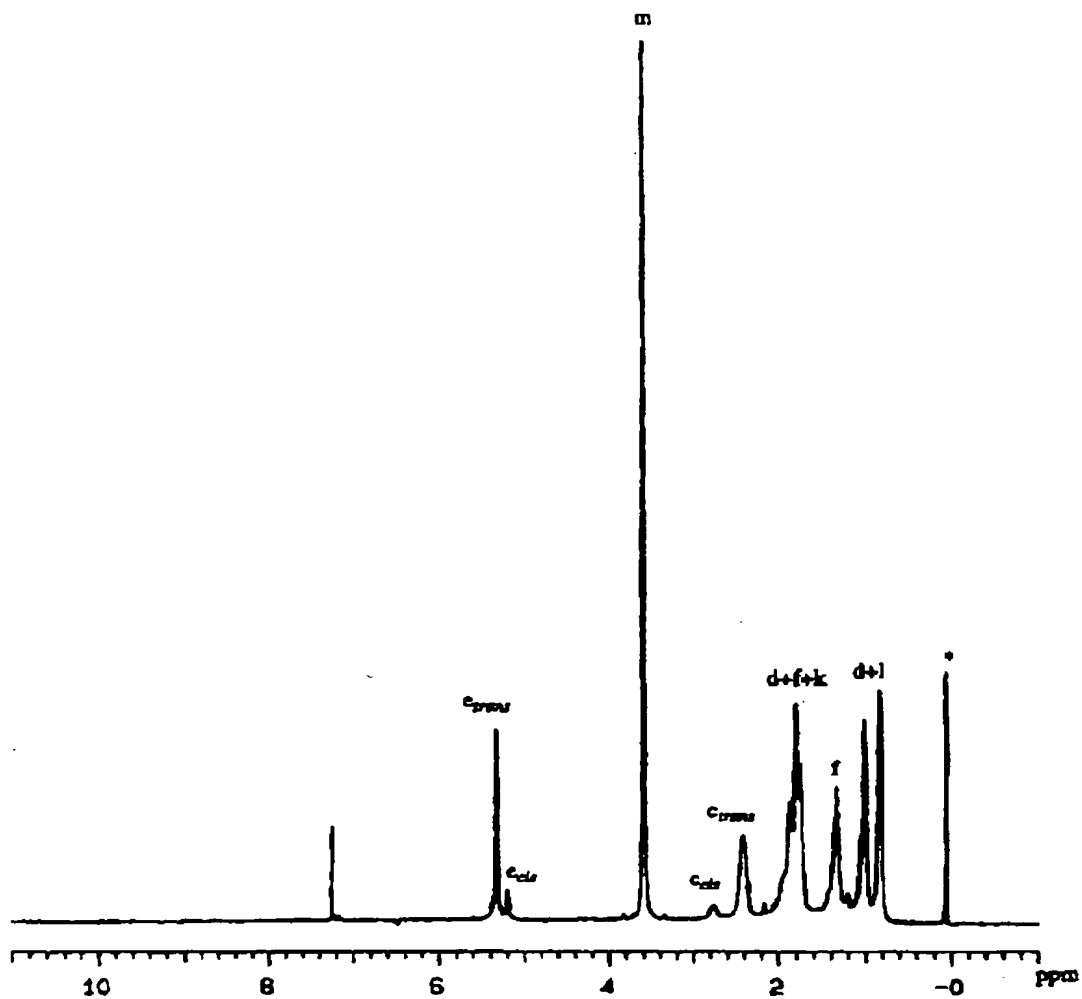
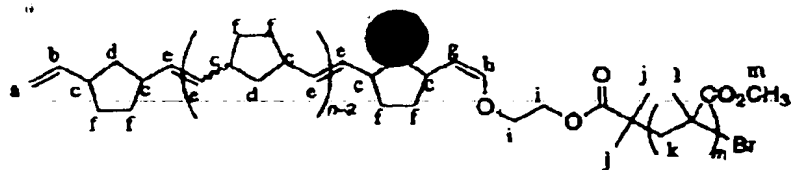


[Drawing 3]

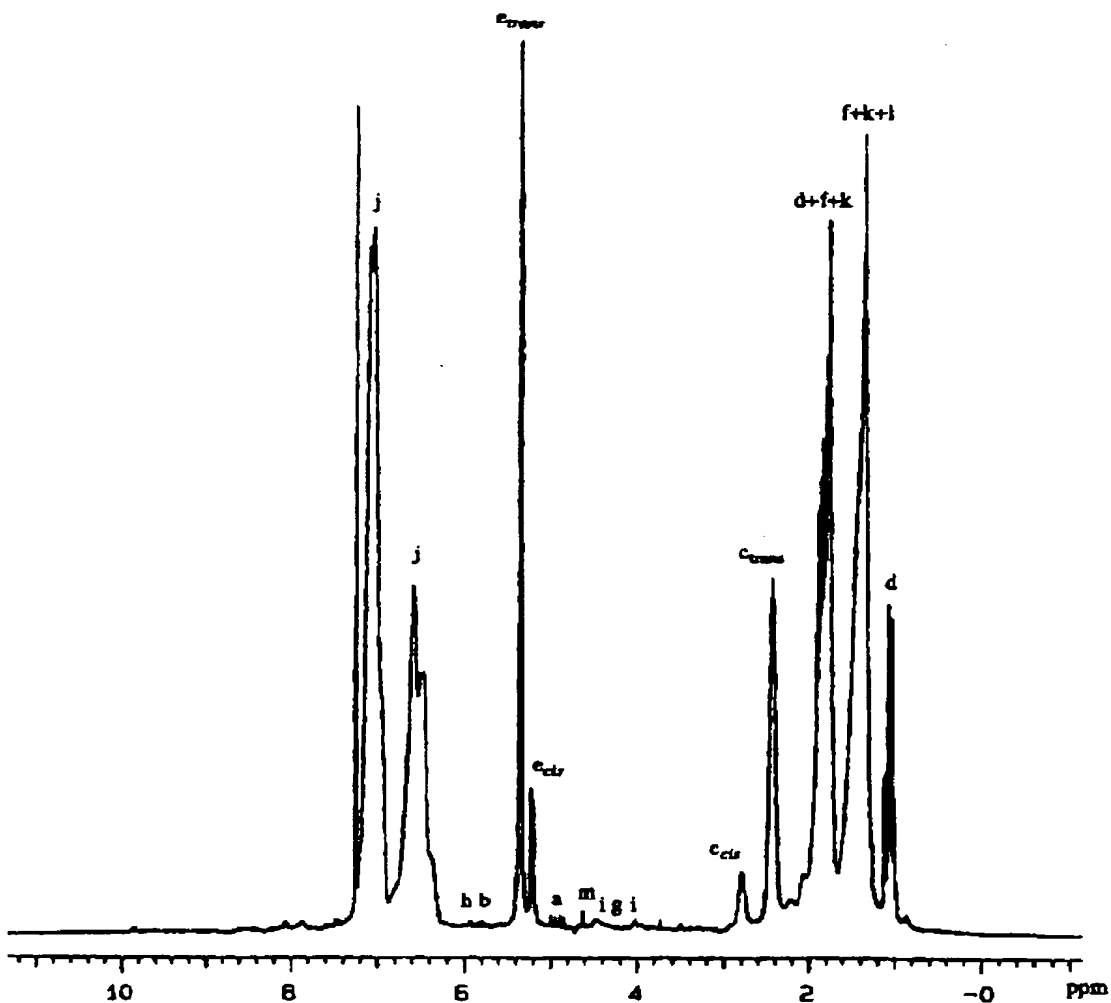
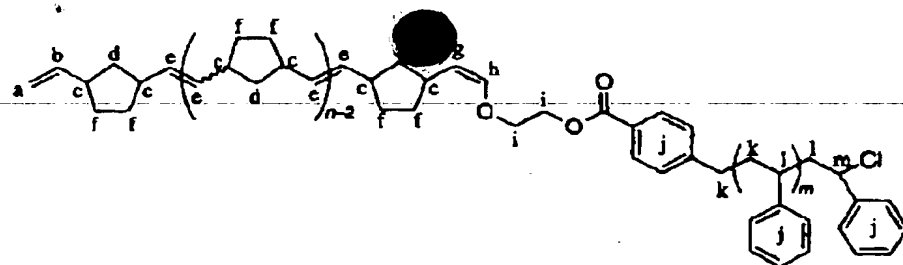




[Drawing 5]



[Drawing 6]



[Translation done.]

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